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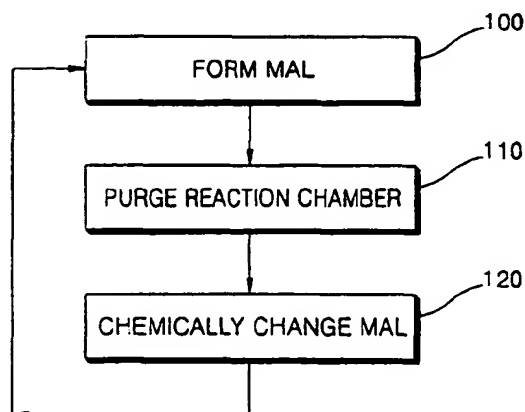
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(54) **Thin film including multi components and method of forming the same**

(57) A thin film including multi components and a method of forming the thin film are provided. A substrate is loaded into a reaction chamber. A unit material layer is formed on the substrate. The unit material layer is a

mosaic atomic layer composed of two kinds of precursors containing components constituting the thin film. The inside of the reaction chamber is purged. The MAL is chemically changed.

**FIG. 3**



## Description

**[0001]** The present invention relates to a thin film and a method of forming the same, and more particularly, to a thin film including multi components composed of unit material layers which are mosaic atomic layers (MALs) composed of components constituting the thin film, and a method of forming the same.

**[0002]** Atomic layer deposition (ALD) is a thin film deposition method which is very different from physical deposition such as electron beam deposition, thermal deposition, or sputter deposition that are generally used. ALD is similar to chemical vapor deposition (CVD) in view of using chemical reaction of reaction gases. However, in general CVD, reaction gases are supplied at the same time and react chemically on the surface of a thin film or in the air. In ALD, different kinds of reaction gases are supplied separately by a time-sharing method, and react with the surface of a thin film. In ALD, if a different kind of reaction gas is supplied when an organic metal compound containing a metallic element (hereinafter referred to as "precursors") is adsorbed on the surface of a substrate, the reaction gas reacts with precursors on the surface of the substrate. As a result, a thin film is formed. Thus, precursors for ALD are not decomposed by themselves at a reaction temperature, and precursors adsorbed on the surface of the substrate must be very rapidly reacted with supplied reaction gas on the surface of the substrate.

**[0003]** ALD can obtain the best uniformity of thickness and step coverage of the thin film from the surface reaction.

**[0004]** The same kinds of precursors are adsorbed on all sites of a wafer surface on which chemisorption is possible. Even if excessive precursors are supplied, the physisorption of the remaining precursors is performed on the chemisorbed precursors. Here, physisorption has less cohesion force than chemisorption. The physisorbed precursors are removed using a purge gas. Different kinds of precursors are supplied and chemisorbed on the chemisorbed precursors. This process is repeated to grow a thin film on the wafer surface at a predetermined speed.

**[0005]** For example, in ALD using precursors A and a reaction gas B, a cycle of supplying precursors A, e.g.,  $N_2$  (or Ar), purging, and supplying a reaction gas B, i.e.,  $N_2$  (or Ar) is repeated to grow a thin film. The growth speed of the thin film represents the thickness of the thin film deposited in one cycle. As a result, the probability that molecules of precursors are adsorbed on any exposed surface is similar, regardless of the roughness of the exposed surface. Thus, if the supply of precursors is sufficient, a thin film having a uniform thickness is deposited at a constant speed regardless of the aspect ratio of the surface structure of the substrate. Also, the thickness and composition of the thin film can be precisely controlled by depositing one layer at a time.

**[0006]** However, ALD also has the following prob-

lems. First, if a thin film containing three components or more is formed, the deposition rate in ALD is lower than the deposition rate in existing CVD.

**[0007]** For example, if an  $SrTiO_3$  layer is formed by ALD, one cycle is composed of eight steps shown in FIG. 1. Precursors containing Sr are supplied in step 10. A purge gas is supplied to purge a reaction chamber for the first time, in step 20. A reaction gas containing oxygen is supplied to oxidize the Sr atomic layer formed in step 10, in step 30. A purge gas is supplied to purge the reaction chamber for the second time, in step 40. Precursors containing Ti are supplied in step 50. A purge gas is supplied to purge the reaction chamber for the third time, in step 60. A reaction gas containing oxygen is supplied to oxidize the Ti atomic layer which is formed in step 50, in step 70. A purge gas is supplied to purge the reaction chamber for the fourth time, in step 80. Thus, the deposition rate in ALD is much lower than the deposition rate in the existing CVD, in which components contained in precursors constituting a thin film are all supplied at the same time.

**[0008]** Second, it is difficult to obtain satisfactory crystal phases of unit material layers constituting a thin film, and thus a subsequent thermal treatment is required. In detail, in FIG. 2, the horizontal axis represents Kelvin temperature K and the vertical axis represents activity. Reference numerals G1 through G11 represent activities of  $TiO_2$ ,  $BaTiO_2$ ,  $SrTiO_3$ ,  $Sr_4Ti_3O_{14}$ ,  $TiO_2S$ ,  $SrCO_3$ ,  $BaCO_3$ ,  $H_2$ ,  $CO_2$ ,  $H_2O$ , and  $Sr_2TiO_4$ , respectively.

**[0009]** Referring to FIG. 2, each phase of SrO and  $TiO_2$  exists stably up to more than 600K if SrO and  $TiO_2$  are alternately stacked by existing ALD to deposit an  $SrTiO_3$  layer. As a result, a desired  $SrTiO_3$  layer can be formed. In other words, the  $SrTiO_3$  layer is only a combined state of SrO and  $TiO_2$ . Thus, an additional thermal treatment is required to change SrO and  $TiO_2$  to a desired crystalline  $SrTiO_3$ . This result is commonly applied to above a ternary thin film. Therefore, the thermal treatment is required to grow an oxide layer of a separate metallic element as a compound layer when the oxide layer is stabilized.

**[0010]** As described above, if a thin film containing three components or more is formed by ALD, an additional thermal treatment is required to form a thin film having a desired crystal structure. Thus, the yield of the thin film process is considerably reduced.

**[0011]** To solve the above-described problems, it is a first object of the present invention to provide a method of forming a thin film including multi components which does not require a subsequent thermal treatment for crystallization, and which has increased yield by forming the thin film at a rapid deposition rate compared to ALD and a crystal phase.

**[0012]** It is a second object of the present invention to provide a thin film formed by the above-described method.

**[0013]** Accordingly, to achieve the first object, there is provided a method of forming a thin film including multi

components. In the method, a substrate is loaded into a reaction chamber. A unit material layer, which is a mosaic atomic layer (MAL) composed of two kinds of precursors containing components constituting a thin film, is formed on the substrate. The inside of the reaction chamber is purged. The MAL is chemically changed. Here, the MAL is formed by supplying the two kinds of precursors at the same time or by a time-sharing method after at least one kind of precursors are less adsorbed on the surface of the substrate than when being saturated.

**[0014]** In this case, first precursors selected from the two kinds of precursors are supplied into the reaction chamber. Next, the reaction chamber is firstly purged and then second precursors selected from the two kinds of precursors are supplied into the reaction chamber.

**[0015]** The reaction chamber is secondly purged, and third precursors selected from the two kinds of precursors are supplied into the reaction chamber.

**[0016]** The first MAL is formed of first and second precursors selected from the two kinds of precursors. The second MAL is formed of first and third precursors selected from the two kinds of precursors.

**[0017]** The second MAL is formed of first and second precursors, of different compositions.

**[0018]** The first MAL is formed by supplying the first and second precursors at the same time or by a time-sharing method

**[0019]** To achieve the first object, there is provided a method of forming a thin film including multi components. The thin film is formed through a first step of loading a substrate into a reaction chamber and sequentially forming a mosaic atomic layer (MAL) composed of two kinds of precursors containing components constituting the thin film and a non-mosaic atomic layer on the MAL to form a unit material layer constituting the thin film on the substrate, a second step of purging the inside of the reaction chamber, and a third step of chemically changing the MAL. Here, the first, second, and third steps constitute one cycle.

**[0020]** In the third step, the resultant material formed in the first step is oxidized by a supplied oxygen source. The following step is performed to remove by-products generated after the oxidation. In other words, an inert gas is made into plasma by supplying the inert gas into the chamber and applying a DC bias to the substrate. As a result, inert gaseous plasma is generated in the chamber, which is used to remove the by-products from the surface of the MAL.

**[0021]** To achieve the second object, there is provided a thin film including multi components, containing at least two components. Here, the thin film is composed of a plurality of unit material layers and each of the unit material layers is a MAL composed of different precursors related to the components. The MALs are double MALs which are composed of first and second MALs.

**[0022]** To achieve the second object, there is provided a thin film including multi components, containing at

least two components. Here, the thin film is composed of a plurality of unit material layers and each of the unit material layers is composed of an MAL, composed of two precursors selected from different precursors related to the components, and a non-mosaic atomic layer composed of any ones selected from the different precursors. The non-mosaic atomic layer is formed on the MAL or the MAL is formed on the non-mosaic atomic layer.

**[0023]** The MAL is a double layer. The double layer may be a MAL composed of a first MAL composed of all of the different precursors and a second MAL composed of two precursors selected from the different precursors, a MAL composed of a first MAL composed of all of the different precursors, or a MAL composed of the same precursors, which have a different composition ratio for each of layers in the double layer.

**[0024]** The double layer is composed of a first MAL, composed of first and second precursors selected from the different precursors, and a second MAL formed on the first MAL, composed of first and third precursors selected from the different precursors.

**[0025]** In the method of forming a thin film including multi components according to the present invention, the advantages of a conventional method of forming ALs can be secured, and fewer steps are required in the process of forming ALs according to the present invention compared to the conventional process of forming ALs. As a result, the time required for forming a thin film can be reduced. Also, since the thin film is formed and crystallized at a low temperature, an additional thermal process for the crystallization of the thin film is unnecessary after the thin film is formed. As a result, the yield of the thin film is remarkably higher than in the prior art.

**[0026]** The above objects and advantages of the present invention will become more apparent by describing in detail preferred embodiments thereof with reference to the attached drawings in which:

FIG. 1 is a flowchart of steps constituting one cycle of a method of forming a thin film including multi components using ALD, according to the prior art;

FIG. 2 is a graph showing results of simulation of thermodynamic equilibrium of an  $\text{SrTiO}_3$  layer, which is one thin film including multi components;

FIG. 3 is a flowchart of steps constituting one cycle of a method of forming a thin film including multi components according to a first embodiment of the present invention;

FIG. 4A is a plan view of a mosaic atomic layer (MAL) which is formed by adsorbing different kinds of components constituting a thin film on the surface of a substrate after a first purge in one cycle of a method of forming the thin film according to the first embodiment of the present invention;

FIG. 4B is a cross-sectional view taken along line b-b' of FIG. 4A;

FIG. 5 is a flowchart of steps constituting one cycle of a method of forming a thin film including multi components according to a second embodiment of the present invention;

FIGS. 6 through 8 are plan views of an atomic layer formed of first precursors containing first components of a thin film, which are chemisorbed on a substrate after a first purge in one cycle of a method of forming a thin film according to the second embodiment of the present invention;

FIGS. 9 through 11 are plan views of a MAL formed of second precursors containing second components of a thin film, which are adsorbed on portions of a substrate between the first precursors containing the first components after a second purge in one cycle of a method of forming a thin film according to the second embodiment of the present invention;

FIG. 12 is a graph explaining a region which is supplied with a source gas for forming a thin film according to the first and second embodiments of the present invention;

FIG. 13 is a view of one cycle of a method of forming a thin film including multi components according to a fifth embodiment of the present invention;

FIGS. 14 and 15 are graphs comparing X-ray diffraction analysis of a thin film formed by a method of forming a thin film including multi components according to the present invention with X-ray diffraction analysis of a thin film formed by a conventional atomic layer deposition method;

FIGS. 16 and 17 are graphs showing carbon content, which is measured to observe the degree of oxidization of a thin film including multi components according to the first and second embodiment of the present invention; and

FIG. 18 through 20 are cross-sectional views of a thin film formed according to first through third embodiments of the present invention.

[0027] Hereinafter, a thin film including multi components and a method of forming the thin film according to embodiments of the present invention will be described in detail with reference to the attached drawings. Here, a substrate is regarded as being loaded into a reaction chamber. Also, the reaction chamber is not specially limited. In other words, any reaction chamber in which an atomic layer may be deposited is possible.

[0028] A method of forming a thin film will be first de-

scribed. Unit material layers of a thin film of the present invention are mosaic atomic layers (MALs), described in first and second embodiments.

#### <First Embodiment>

[0029] Referring to FIG. 3, MALs, which are unit material layers of a thin film, are formed on a substrate in step 100. The MALs are formed of precursors containing components constituting the thin film. Thus, if the thin film is formed of three components, the MALs are formed of three precursors each containing the three components. If the thin film is formed of four or more components, the MALs are formed of four or more precursors each containing the four or more components.

[0030] To form the MALs, all components constituting the thin film are supplied into a reaction chamber, in a predetermined amount in consideration of the composition ratio of the components, and chemisorbed on the substrate. The MALs are single atomic layers composed of a plurality of components constituting the thin film.

[0031] As a detailed example of forming the MALs, if the thin film is a three component system oxide layer, e. g., a STO layer, the MALs are formed of a precursor containing Sr and a precursor containing Ti. In other words, a predetermined amount of the precursor containing Sr and a predetermined amount of the precursor containing Ti are supplied into the reaction chamber at a time. Here, it is preferable that the two precursors are supplied in a smaller amount than when the two precursors each form an atomic layer. This will be described later.

[0032] If the thin film is a BST layer containing three metal elements, the MALs are formed by supplying a predetermined amount of a precursor containing Ba, a predetermined amount of a precursor containing Sr, and a predetermined amount of a precursor containing Ti into the reaction chamber at a time. Here, it is preferable that the substrate is maintained at a predetermined reaction temperature so that the three precursors are chemisorbed on the substrate.

[0033] The thin film may be an oxide layer, a nitride layer, or a boride layer, as well as the STO layer and the BST layer. For example, the thin film may be a PZT layer, a YBCO layer, a SBTO layer, a HfSiON layer, a ZrSiO layer, a ZrHfO layer, a LaCoO layer, or a TiSiN layer.

[0034] If the thin film is an oxide layer, a nitride layer, or a boride layer, the MALs are not oxidized, nitrified, or boronized. Thus, the MALs are oxidized, nitrified, or boronized in a subsequent process. This will be described later.

[0035] Precursors remaining after the MALs are formed on the substrate may be physisorbed on the MALs. The precursors physisorbed on the MALs may serve as particles in a subsequent process and prevent the MALs from being oxidized, nitrified, or boronized in a subsequent oxidation, nitrification, or boronization process. Thus, it is preferable that the precursors physisorbed on the MALs are removed. To remove the pre-

cursors physisorbed on the MALs, the reaction chamber is purged using an inert gas, e.g., a nitride gas or an argon gas, after the MALs are formed in step 110. As a result, the MALs, which are unit material layers constituting the thin film, remain as single atomic layers on the substrate. This is shown in FIG. 4.

**[0036]** FIG. 4A is a plan view of the MALs and FIG. 4B is a cross-sectional view taken along line b-b' of FIG. 4A. Reference numerals 130, 132, and 134 represent precursors containing first components constituting a thin film, precursors containing second components constituting the thin film, and a substrate, respectively. In FIGS. 4A and 4B, it is seen that the MALs may be formed of different precursors 130 and 132 each containing different components constituting the thin film.

**[0037]** The MALs are chemically changed by supplying a predetermined reaction gas into the reaction chamber in step 120. For example, the MALs are oxidized, nitrified, or boronized. Here, the substrate is heated to a predetermined temperature to react the reaction gas with the MALs.

**[0038]** The reaction gas may be supplied with external energy to lower the temperature for heating the substrate and increase the reaction activity of the reaction gas. The method of oxidizing, nitrifying, or boronizing the MALs depends on the method of supplying the external energy. For example, when the MALs are oxidized, radio frequency (RF) energy, a DC voltage, or microwave energy is applied to a reaction gas such as O<sub>2</sub>, O<sub>3</sub>, H<sub>2</sub>O, and H<sub>2</sub>O<sub>2</sub> containing oxygen during the supply of the reaction gas into the reaction chamber. Thus, the reaction gas is plasmatized. As a result, the MALs are oxidized using plasma.

**[0039]** If the external energy is ultraviolet, the MALs are oxidized by a reaction of decomposing O<sub>3</sub> under ultraviolet. In other words, the MALs are oxidized in an ultraviolet-ozone process.

**[0040]** After the chemical change of the MALs is completed, first through third steps from forming to chemically changing the MALs are repeated until the MALs are formed to a desired thickness.

#### <Second Embodiment>

**[0041]** Unit material layers of a thin film are formed as MALs on a substrate by supplying components constituting the thin film by a time-sharing method. Here, the thin film is the same as the thin film described in the first embodiment.

**[0042]** Referring to FIG. 5, first atomic layers (hereinafter, referred to as "first discrete atomic layers") are formed of precursors which are spaced apart from each other, in step 200. In detail, conventional atomic layers are formed to completely cover the entire surface of the substrate (on the entire surface of the structure if a structure is formed on the substrate). Thus, the conventional atomic layers are continuous atomic layers. However, precursors containing first components of components

constituting a thin film are discrete on the substrate to form the first discrete atomic layer. Here, the precursors are uniformly discrete on the entire surface of the substrate. Second components constituting the thin film, which will be supplied later, may be uniformly chemisorbed between the first components. Here, it is preferable that the substrate is maintained at a reaction temperature so that the supplied components are chemisorbed on the substrate. The components may be heated to the reaction temperature or a temperature close to the reaction temperature, in the course of being supplied.

**[0043]** FIG. 6A is a plan view of the first discrete atomic layer formed of precursors containing the first components and FIG. 6B is a cross-sectional view taken along line b-b' of FIG. 6A. Here, reference numeral 202 represents the first discrete atomic layer, reference numeral 204 represents precursors (hereinafter, referred to as "first precursors") containing the first components constituting the first discrete atomic layer, and reference numeral 206 represents a substrate on which the first discrete atomic layer 202 is chemisorbed. A thin film, which is formed on the substrate 206, contains at least three components. At least two of the three components are chemisorbed on the substrate 206.

**[0044]** For example, if the thin film is a thin film including multi components such as an SrTiO<sub>3</sub> layer or a BaTiO<sub>3</sub> layer containing three components, the first precursors 204 contain strontium (Sr), barium (Ba), or Titanium (Ti). The first discrete atomic layer 202 is formed by chemisorbing the precursors containing strontium (Sr) or barium (Ba) on the substrate 206.

**[0045]** Steps of forming the thin film containing the three components are also applied to a thin film containing four components. Here, if an oxygen component is contained in the four components, the first precursors 204 contain any of the other four components (i.e. not the oxygen component). The first discrete atomic layer 202 is formed by being uniformly discrete and chemisorbed the precursors on the substrate.

**[0046]** As shown in FIG. 6B, unlike the precursors constituting the conventional continuous atomic layers, the first precursors 204 constituting the first discrete atomic layer 202 are widely discrete on the substrate 206. Reference numeral 208 represents second precursors, which will be formed between the first precursors 204 in a subsequent process.

**[0047]** The distribution of the first precursors 204 may vary, depending on the kinds of first precursors 204 and second precursors 208. For example, as shown in FIGS. 7 and 8, the first discrete atomic layer 202 may have a structure in which precursors are arranged in an oblique line, or in which precursors are arranged in a hexagonal shape with one precursor in the center.

**[0048]** The characteristics of the shape of the first discrete atomic layer 202, i.e., the distance between the first precursors 204, is determined by the supplied amount of the first precursors 204. For example, if the

thin film is an  $\text{SrTiO}_3$  layer, the first discrete atomic layer 202 is formed of Sr precursors. Also, the distribution of the first discrete atomic layer 202 is determined by the amount of Sr precursors supplied into the reaction chamber. Preferably, the Sr precursors are supplied in a smaller amount than Sr precursors supplied to form an  $\text{SrTiO}_3$  layer by a conventional method of forming an atomic layer.

[0049] In detail, G12 of FIG. 12 is a graph showing changes in the amount of Sr precursors with respect to time when an  $\text{SrTiO}_3$  layer is formed by the conventional method of an atomic layer. Reference numeral S represents a saturated region. The saturated region S represents a region in which a sufficient amount of the Sr precursors is supplied so that the Sr precursors are adsorbed on the entire surface of the substrate. Reference numeral  $S_0$  is an initial region, in which the supply of Sr precursors begins, and becomes the saturated region S as time passes. Thus, the amount of Sr precursors supplied in the initial region  $S_0$  is smaller than the amount of Sr precursors supplied in the saturated region S. As a result, the substrate is not completely covered with only the amount of Sr precursors supplied in the initial region  $S_0$ . There is no cause for the Sr precursors to be adsorbed onto a particular region only of the substrate during the supply of Sr precursors into the reaction chamber. In other words, the probability that the Sr precursors supplied into the reaction chamber are adsorbed on any particular region of the substrate in any one step is equivalent to the Sr precursors. As a result, the Sr precursors supplied in the initial region  $S_0$  are discrete on the substrate.

[0050] The first discrete atomic layer 202 containing the first components having various distribution shapes as described above may be formed by controlling the amount of precursors supplied on the substrate in the initial region  $S_0$ . Vacant regions 208, on which second precursors containing second components may be adsorbed, exist between the first precursors 204 on the substrate.

[0051] As described above, the shape of the first discrete atomic layer 202 may be determined by limiting the amount of precursors supplied into the reaction chamber to that of the initial region  $S_0$ . Even in this case, it is preferable that the amount of precursors required for forming the first discrete atomic layer 202 containing the first components varies according to the number of components constituting the thin film, the composition ratio of the components, and the order of forming the components, i.e. which component is first formed.

[0052] For example, supposing that the first discrete atomic layer 202 containing the first components is formed during the formation of a thin film containing three components, and reference numeral  $A_N$  of FIG. 12 represents the amount of precursors. The amount of precursors supplied for forming an initial atomic layer on a substrate during the formation of a thin film containing four or more components may be smaller than or equal

to the amount  $A_N$  depending on which one of the four components the initial atomic layer contains, i.e., the composition of a component contained in the precursors constituting the initial atomic layer occupying the four components.

[0053] Referring to FIG. 5, the reaction chamber is purged for the first time, in step 300. It is preferable that the first precursors 204 are all used in forming the first discrete atomic layer 202 containing the first components. However, a portion of the first precursors 204 may not be used in forming the first discrete atomic layer 202. If the first precursors 204 remain in the reaction chamber, the first precursors 204 are mixed with other precursors that may be supplied later. As a result, a thin film having an unwanted shape may be formed. Thus, it is preferable that any of the first precursors 204 which are not used in forming the first discrete atomic layer 202 are discharged from the reaction chamber. In other words, the reaction chamber is purged using an inert gas which does not react chemically, to discharge precursors not used in forming the first discrete atomic layer 202. Here, the inert gas is Ar,  $\text{N}_2$ , or  $\text{O}_2$ .

[0054] A second discrete atomic layer composed of precursors containing second components is formed in step 400. Here, the precursors (hereinafter, referred to as "second precursors") constituting the second discrete atomic layer are chemisorbed on portions of the substrate between the first precursors.

[0055] In detail, after the first purge in step 300, a predetermined amount of the second precursors is supplied into the reaction chamber. Here, the second precursors contain the second components, which are selected from components constituting the thin film, and may be chemisorbed on the substrate.

[0056] For example, if the thin film is a  $\text{SrTiO}_3$  layer or a  $\text{BaTiO}_3$  layer, the second precursors contain Ti. If the first precursors 204 contain Ti, the second precursors contain Sr or Ba. This may be applied to a thin film containing four or more components, three or more components of which are adsorbed on the substrate.

[0057] It is preferable that the second precursors are supplied in consideration of the following. If the second precursors contain the last one of the components contained in the thin film which are chemisorbed on the substrate, it is preferable that the second precursors are sufficiently supplied so that the second precursors are all adsorbed on vacant regions of the first discrete atomic layer 202 containing the first components, i.e., on regions of the substrate on which the first precursors are not adsorbed.

[0058] If the second precursors do not contain the last component, third and fourth precursors which are chemisorbed are continuously supplied after the second precursors are supplied. Thus, it is preferable that first precursors are supplied in an amount sufficient for leaving predetermined vacant regions on the substrate between the first precursors on which subsequent precursors are chemisorbed. As a result, subsequent precursors may

be chemisorbed between the first and second precursors even though the first and second precursors are adsorbed on the substrate. Thus, in the latter case, it is preferable that the second precursors are supplied in the amount supplied in the initial region  $S_0$  (Refer to FIG. 12) as when the first precursors are supplied. However, the second precursors may be supplied in a larger or smaller amount than the first precursors, according to the composition ratio of the components contained in the second precursors accounting for the thin film. In a case where the component ratio of the components contained in the first precursors is identical to the component ratio of the components contained in the second precursors, and only the first and second precursors are restricted as being chemisorbed, it is preferable that the amount of the first precursors and the amount of the second precursors are equal in the initial region  $S_0$ . A mosaic atomic layer (MAL) 210, which is composed of the first precursors 204 constituting the first discrete atomic layer 202 and the second precursors 208 constituting the second discrete atomic layer (and may be the same as the first discrete atomic layer 202 shown in FIG. 4), is formed on the substrate 206 as a unit material layer constituting the thin film, through the steps 200, 300, and 400 as shown in FIG. 6. If the MAL 210 is formed of only the first and second precursors 204 and 208, it is preferable that the first and second precursors 204 and 208 contact each other. However, in FIG. 9, the first and second precursors 204 and 208 are shown spaced apart from each other for convenience. This is applied to various examples of the MAL 210 due to various arrangement shapes of the first precursors 204 shown in FIGS. 10 and 11.

[0059] The reaction chamber is purged for the second time, in step 400. In other words, for the same reason as in step 300, the reaction chamber is purged using an inert gas after the MAL 210 is formed.

[0060] The MAL 210 is chemically changed in step 600. In other words, the MAL 210 is oxidized, nitrified, or boronized using several reaction gases. When bulky ligands are decomposed and removed due to this chemical reaction, new chemisorbed points which were covered by the ligands may be exposed.

[0061] To oxidize the MAL 210, reaction gas such as  $O_2$ ,  $O_3$ ,  $H_2O$ , and  $H_2O_2$  is supplied into the reaction chamber in a predetermined amount and reacts with the MAL 210. Here, when the reaction gas is supplied into the reaction chamber, radio frequency (RF) or microwave energy, or a DC voltage, may be applied to the reaction gas, to increase the activity of the reaction gases. Thus, the reaction gas may form plasma in the reaction chamber. If the reaction gas is ozone, ultraviolet (UV) is applied to the reaction gas to increase the activity of the reaction gas. In other words, the MAL 210 is oxidized using UV- $O_3$ .

[0062] The reaction chamber is purged for the third time, in step 700. The gases remaining in the reaction chamber after step 500 are purged using the inert gas.

[0063] Steps 200, 300, 400, 500, 600, and 700 are repeated until the thin film is formed to a desired thickness.

[0064] If third and fourth precursors are further chemisorbed on the substrate after the second purge in step 500, i.e., if the thin film is not a nonoxide layer containing at least three components or an oxide layer containing four or more components, a step of forming an atomic layer composed of third precursors containing third components, a third purge step, a step of forming an atomic layer composed of four precursors containing four components, and a fourth purge step, are sequentially performed before step 700.

[0065] When the formation of the MAL is repeated to form the thin film, the compositions of the formed MALs may be different from each other. In other words, when components constituting a subsequent MAL are the same as components constituting former MAL, the composition of any one of precursors constituting the two MALs, i.e., the composition of any one of components constituting the thin film, may be different from the compositions of the other components.

[0066] For example, if the thin film is a STO layer having a predetermined thickness, the STO layer may be formed to a desired thickness by repeatedly forming a unit material layer composed of Sr precursors and Ti precursors, i.e., an Sr-Ti MAL. However, if three Sr-Ti MALs are sequentially formed to form the STO layer, the composition of precursors constituting a second or third Sr-Ti MAL may be different from the composition of precursors constituting a first Sr-Ti MAL. This composition may be controlled by controlling the amount of precursors supplied into the reaction chamber.

[0067] The second discrete atomic layer 210 may be formed by supplying the second precursors two times in step 400. In other words, the second discrete atomic layer is not completely formed by supplying the second precursors only one time. Thus, the second precursors are supplied for the first time in a predetermined amount to form the second discrete atomic layer. Next, purging is performed, and then the second precursors are supplied for the second time in a predetermined amount, to complete the second discrete atomic layer. If the second discrete atomic layer is not completely formed after the second precursors are supplied for the second time, the second precursors may be supplied for the third time. Also, the amount of the second precursors may be different in the first and second supplies.

[0068] This method may be applied to the thin films containing three or more components described in the first embodiment as well as the STO layer.

#### <Third Embodiment>

[0069] A unit material layer is formed of a double MAL. In detail, if a thin film to be formed contains at least three components, the three components are divided into two and the two are each formed as MALs.



[0070] For example, if the thin film contains three components, i.e.,  $A_{1-x-y}B_xC_y$ , a first MAL ( $A_{1-x}B_x$ ) composed of precursors containing a component A (hereinafter, referred to as "precursors A") and precursors containing a component B (hereinafter, referred to as "precursors B") is formed on a substrate. Next, a second MAL ( $A_{1-y}C_y$ ) composed of the precursors A and precursors containing a component C (hereinafter, referred to as "precursors C") is formed on the first MAL ( $A_{1-x}B_x$ ). Here, the first and second MALs may be formed according to the first and second embodiments. Also, the first MAL may be oxidized before the second MAL is formed so that the second MAL is chemisorbed on the first MAL. The first MAL is oxidized according to the oxidation process described in the first or second embodiment. It is preferable that purging is performed among the steps of forming the second MAL. After the second MAL is formed, the second MAL is oxidized according to the process of oxidizing the first MAL. Thus, the first and second MALs are a unit material layer constituting the thin film. Next, the processes of forming the first and second MALs are repeated on the oxidized second MAL, to form the thin film to a desired thickness.

[0071] The thin film formed by the method of forming a thin film according to the third embodiment of the present invention may correspond to all of the thin films described in the process of forming a thin film according to the first embodiment.

[0072] As an example, if the thin film is a PZT layer, precursors A, B, and C represent precursors containing Pb, precursors containing Zr, and precursors containing Ti, respectively. The first and second MALs are a MAL composed of the precursors containing Pb and Zr and a MAL composed of the precursors containing Pb and Ti, respectively. Also, if the thin film is a BST layer, the precursors A, B, and C represent precursors containing Ba, precursors containing Sr, and precursors containing Ti, respectively, and the first and second MALs are a MAL composed of the precursors Ba and Sr and a MAL composed of the precursors containing Ba and Ti, respectively.

#### <Fourth Embodiment>

[0073] A thin film is formed of unit material layers, a portion of which is MALs and the others are atomic layers (ALs) on the MALs. In other words, unit material layers constituting the thin film are formed of MALs and ALs. Here, the ALs are non-mosaic atomic layers.

[0074] In detail, if the thin film contains three or more components, e.g., components A, B, and C as described in the third embodiment, a MAL is formed of precursors A and B each containing the components A and B on a substrate to form the thin film. Here, the MAL is formed by the methods described in the first, second, and third embodiments. Next, a reaction chamber is purged. An AL is formed of the precursors C containing the component C on the MAL. Here, it is preferable that the AL is

formed, preferably chemisorbed, after the MAL is oxidized as described in the second embodiment.

[0075] Thus, the unit material layer is formed of the MAL composed of the precursors A and B and the AL composed of the precursors C on the substrate. The MAL may be formed of the precursors A and C instead of the precursors A and B. Thus, the AL may be formed of the precursors B.

[0076] The AL is formed of the precursors C on the MAL and oxidized by the same method as when oxidizing the MAL. The thin film is formed to a desired thickness by repeating former steps on the oxidized AL.

#### <Fifth Embodiment>

[0077] An oxidization gas or a deoxidization gas is supplied to react a MAL with chemically adsorbed precursors in a process of forming the MAL containing at least two kinds of components, e.g., Sr and Ti. By-products generated in this process, e.g., hydrocarbon-based by-products, may exist on the surface of the MAL.

[0078] In a process of forming a thin film including multi components containing at least two kinds of metallic atoms using a MAL process or an ALD process, it is difficult to perform a subsequent cycle of the MAL process or the ALD process due to these by-products. Thus, it is necessary to remove the by-products, and the fifth embodiment of the present invention pertains to this.

[0079] In detail, referring to FIG. 13, three steps are sequentially performed: supplying a source gas to form the MAL (500); firstly purging remainder that is not adsorbed after the supply of the source gas (510); and supplying a reaction gas (a oxidization or deoxidisation gas) to oxidize or deoxidize the MAL (520). Thereafter, a second purge step 530 is performed to remove by-products generated due to the reaction of the MAL and the reaction gas. In the second purge step 530, a purge gas as is an inert gas such as Ar, He, Ne, or  $N_2$ . In the second purge step 530 using the purge gas, DC-bias is applied to the substrate to increase of an efficiency of removing the by-products so as to make the inert gas into plasma. In other words, inert gaseous plasma is generated and used as the purge gas in the second purge step 530. Positive ions of the inert gaseous plasma bombard against the surface of the MAL, which results in the removal of the by-products adsorbed on the surface of the MAL.

[0080] As described above, a thin film which is less contaminated by impurities can be formed by using the inert gaseous plasma as the purge gas after the supply of the reaction gas. In particular, the bombardment of ions having high energy against the by-products adsorbed on the surface of the MAL can achieve a high temperature deposition effect although the thin film is deposited at a low temperature.

[0081] The fifth embodiment of the present invention, as described above, can be applied to the ALD process



containing two kinds of components as well as the MAL deposition process.

[0082] X-ray diffraction analysis of a thin film formed by a method of forming a thin film including multi components according to the present invention and of a thin film formed by a conventional atomic layer deposition method will be described. Here, the thin films including multi components are  $\text{SrTiO}_3$  layers.

[0083] In detail, FIG. 14 shows the results of X-ray diffraction analysis of a thin film formed according to the prior art, and FIG. 15 shows the results of X-ray diffraction analysis of a thin film formed according to the present invention.

[0084] In FIG. 14, peaks due to ruthenium (Ru) and silicon (Si) are shown, and in FIG. 15, peaks due to ruthenium (Ru), silicon (Si), and  $\text{SrTiO}_3$  are shown. Reference numeral Ps is the peak due to  $\text{SrTiO}_3$ .

[0085] In the prior art, there are no peaks showing the crystallization of the thin film including multi components. In the present invention, there are peaks showing the crystallization of the thin film including multi components.

[0086] Accordingly, unlike the prior art, after a thin film including multi components is formed according to the embodiments of the present invention, an additional thermal treatment for the crystallization of the thin film is unnecessary.

[0087] FIGS. 16 and 17 are graphs showing the analysis of titanium content after a titanium layer is formed on a substrate and oxidized, to observe the possibility of oxidization of a thin film including multi components according to the first through fourth embodiments of the present invention. FIG. 16 shows the result after a titanium atomic layer is formed on a substrate, a titanium layer is physisorbed on the titanium atomic layer, and a process of oxidizing the resultant structure is repeated. FIG. 17 shows the result after a titanium atomic layer is formed on a substrate and a process of oxidizing the resultant structure is repeated. In FIGS. 16 and 17, reference numerals Go, Gti, Gsi, and Gc represent changes in the contents of oxygen, titanium, silicon, and carbon, respectively. Here, it is noted that the whole titanium layer is oxidized on a substrate, and carbon component is less than 0.5%. From this result, it is noted that the first and second MALs may be formed and fully oxidized at the same time. Also, at least two MALs may be formed on the substrate and oxidized at the same time, for a cycle by which an atomic layer is formed on the substrate.

[0088] A thin film formed by a method of forming a thin film according to an embodiment of the present invention will be described.

#### <First Embodiment>

[0089] As shown in FIG. 18, a thin film 800 is formed of a plurality of unit material layers L on a substrate 206. The unit material layers L are composed of first compo-

nents P1 and second components P2. Here, the thin film 800 is an oxide layer, a nitride layer, or a boride layer. The thin film may be a STO layer, a PZT layer, a BST layer, a YBCO layer, a SBTO layer, a  $\text{HfSiON}$  layer, a  $\text{ZrSiO}$  layer, a  $\text{ZrHfO}$  layer, a  $\text{LaCoO}$  layer, or a  $\text{TiSiN}$  layer.

[0090] The unit material layers L are preferably MALs composed of components of which the thin film is composed. Thus, if the thin film is composed of first through third components, the unit material layers L are MALs which are composed of the first through third components. If the thin film is composed of first through fourth components, the unit material layers L are MALs which are composed of the first through fourth components.

#### <Second Embodiment>

[0091] In the second embodiment, a thin film is formed of three components having a predetermined composition. As shown in FIG. 19, a thin film 900 is formed of a plurality of unit material layers L1, which are each double MALs. In other words, a unit material layer L1 is composed of a first MAL L1a and a second MAL L1b, which are sequentially formed. The first MAL L1a is composed of first components P21 and second components P22 of which the thin film 900 is composed. The second MAL L1b is composed of the first components P21 and third components P23, of which the thin film 900 is composed.

#### <Third Embodiment>

[0092] As shown in FIG. 20, a thin film 1000 is formed of unit material layers L2 which are composed of MALs L2a and atomic layers L2b. The MALs L2a are composed of first and second components P31 and P32 of which the thin film 1000 is formed, and the atomic layers L2b are composed of third components P33 of which the thin film 1000 is formed.

[0093] In the first through third embodiments, any one of a single MAL L and a double MAL L1 constituting a unit material layer of a thin film, or the MAL L2a and an atomic layer L2b constituting a unit material layer of a thin film, is an atomic layer composed of at least two different components. Thus, though is not shown in FIGS. 18 through 20, MALs constituting unit material layers of a thin film according to each of the first through third embodiments may be mosaic atomic layers composed of (precursors containing) three or four different components depending on the number of components constituting the thin film.

[0094] As described above, in the method of forming a thin film including multi components according to the present invention, unit material layers constituting a thin film are formed of single MALs or double MALs containing components of which at least one is different from the others. The unit material layers may be composed of MALs and ALs containing only one of the components

constituting the thin film. Thus, the advantages of a conventional method of forming ALs can be secured, and fewer steps are required in the process of forming ALs according to the present invention compared to the conventional process of forming ALs. As a result, the time required for forming a thin film can be reduced. Also, since the thin film is formed and crystallized at a low temperature, an additional thermal process for the crystallization of the thin film is unnecessary after the thin film is formed. As a result, the yield of the thin film is remarkably higher than in the prior art.

[0095] Although many contents have been described above, they must be construed as examples of preferred embodiments of the present invention rather than restricting the scope of the present invention. For example, if the number of components constituting a thin film is large, the thin film may be formed by a dual method by one of ordinary skill in the art. In other words, instead of forming and oxidizing MALs containing components constituting thin film, MALs containing a portion of the components are formed, i.e., at least two MALs are formed and oxidized. Next, MALs containing the other components are formed and oxidized. Also, another embodiment, which is not described in the detailed description, may be realized by a combination of the methods according to the embodiments of the present invention. For example, a first MAL may be formed on a substrate by a method of forming a thin film according to a first embodiment of the present invention. Any one of subsequent MALs may be formed by a method of forming a thin film according to a second embodiment of the present invention.

## Claims

1. A method of forming a thin film including multi components, the method comprising:
  - loading a substrate into a reaction chamber, forming a unit material layer, which is a mosaic atomic layer (MAL) composed of two kinds of precursors containing components constituting a thin film, on the substrate;
  - purging the inside of the reaction chamber; and chemically changing the MAL.
2. The method according to claim 1, wherein the MAL is formed by simultaneously supplying the two kinds of precursors.
3. The method according to claim 1, wherein the MAL is formed by sequentially supplying the two kinds of precursors by a time-sharing method.
4. The method according to claim 3, further comprising:

supplying first precursors selected from the two kinds of precursors into the reaction chamber; firstly purging the reaction chamber; and supplying second precursors selected from the two kinds of precursors into the reaction chamber.

5. The method according to claim 3, wherein each of the first and second precursors is supplied in an amount less than that sufficient for forming an atomic layer on the entire surface of the substrate.
6. The method according to claim 4, further comprising:
  - secondly purging the reaction chamber; and supplying third precursors selected from the two kinds of precursors into the reaction chamber.
7. The method according to any of claims 1 to 6, wherein the MAL is a double MAL composed of first and second MALs.
8. The method according to claim 7, wherein the first MAL is chemically changed before the second MAL is formed on the first MAL.
9. The method of according to claim 7 or 8, wherein the first MAL is formed of first and second precursors selected from the two kinds of precursors.
10. The method according to any of claims 7 to 9, wherein the second MAL is formed of first and third precursors selected from the two kinds of precursors.
11. The method according to any of claims 7 to 9, wherein the second MAL is formed of first and second precursors, of different compositions.
12. The method according to any of claims 1 to 11, wherein in chemically changing the MAL, the MAL is oxidized, nitrified, or boronized.
13. The method according to claim 12, wherein the MAL is oxidized using plasma or ultraviolet-ozone using either  $H_2O$ ,  $O_2$ ,  $O_3$ , or  $H_2O_2$  as a source of oxygen.
14. The method according to claim 17, wherein the source of oxygen is purged using an inert gas, wherein DC-bias is applied to the substrate to make the inert gas into plasma so as to form inert gaseous plasma which is used to remove by-products adsorbed on the surface of the MAL.
15. The method according to claim 13, wherein the plasma is formed using radio frequency (RF) or mi-

- crowave energy.
16. The method according to any of claims 7 to 15, wherein the first MAL is chemically changed by either an oxidation method, a nitrification method, or a boronization method. 5
  17. The method according to any of claims 4 to 16, wherein additional second precursors are supplied after the second precursors are supplied. 10
  18. The method according to any of claims 6 to 17, wherein additional third precursors are supplied after the third precursors are supplied. 15
  19. The method according to any of claims 1 to 18, wherein the thin film is either an oxide layer, a nitride layer, or a boride layer.
  20. The method according to any of claims 1 to 18, wherein the thin film is an STO layer, a PZT layer, a BST layer, a YBCO layer, an SBTO layer, a HfSiON layer, a ZrSiO layer, a ZrHfO layer, a LaCoO layer, or a TiSiN layer. 20
  21. A method according to any of claims 1 to 20, wherein the substrate is loaded into the reaction chamber and a mosaic atomic layer (MAL) subsequently formed composed of two kinds of precursors containing components constituting the thin film and a non-mosaic atomic layer on the MAL to form a unit material layer constituting the thin film on the substrate. 25
  22. The method according to any of claims 13 to 21, wherein the source of oxygen is purged using an inert gas, wherein the inert gas is made into plasma to form inter gaseous plasma which is used to remove by-products adsorbed on the surface of the MAL. 30
  23. The method according to claim 21 or 22, wherein when the MAL is formed by supplying the two kinds of precursors by a time-sharing method, each of the two kinds of precursors is supplied in an amount less than that sufficient for covering the entire surface of the substrate. 35
  24. A thin film including multi components, containing at least two components, wherein the thin film is composed of a plurality of unit material layers and each of the unit material layers is a mosaic atomic layer (MAL) composed of different precursors related to the components. 40
  25. The thin film including multi components according to claim 24, wherein the MALs are double MALs which are composed of first and second MALs. 45
  26. The thin film including multi components according to claim 25, wherein the first and second MALs are formed of the same precursors, which have a different composition ratio for each of the first and second MALs. 50
  27. The thin film including multi components according to claim 25 or 26, wherein the first MAL is composed of first and second precursors selected from the different precursors. 55
  28. The thin film including multi components according to any of claims 25 to 27, wherein the second MAL is composed of the first precursors and third precursors selected from the different precursors.
  29. The thin film including multi components according to any of claims 24 to 28, wherein the thin film is either an oxide layer, a nitride layer, or a boride layer.
  30. The thin film including multi components according to any of claims 24 to 28, wherein the thin film is selected from an STO layer, a PZT layer, a BST layer, a YBCO layer, an SBTO layer, a HfSiON layer, a ZrSiO layer, a ZrHfO layer, a LaCoO layer, and a TiSiN layer.
  31. A thin film including multi components according to any of claims 24 to 30, wherein the thin film is composed of a plurality of unit material layers and each of the unit material layers is composed of an MAL, composed of two precursors selected from different precursors related to the components, and a non-mosaic atomic layer composed of any ones selected from the different precursors.
  32. The thin film including multi components according to claim 31, wherein the non-mosaic atomic layer is formed on the MAL.
  33. The thin film including multi components according to claim 31, wherein the MAL is formed on the non-mosaic atomic layer.
  34. The thin film including multi components according to any one of claims 31 to 33, wherein the MAL is a double layer.
  35. The thin film including multi components according to claim 34, wherein the MAL is composed of a first MAL composed of all of the different precursors and a second MAL composed of two precursors selected from the different precursors.
  36. The thin film including multi components according to claim 34, wherein the MAL is composed of a first MAL composed of all of the different precursors.

37. The thin film including multi components according to claim 34, wherein the double layer is composed of the same precursors, which have a different composition ratio for each of layers in the double layer. 5
38. The thin film including multi components according to any of claims 34 to 37, wherein the double layer is composed of a first MAL, composed of first and second precursors selected from the different precursors, and a second MAL formed on the first MAL, 10 composed of first and third precursors selected from the different precursors.
39. The thin film including multi components according to any of claims 31 to 38 wherein the thin film is an oxide layer, a nitride layer, or a boride layer. 15
40. The thin film including multi components according to any of claims 31 to 38, wherein the thin film is selected from an STO layer, a PZT layer, a BST layer, a YBCO layer, an SBT layer, a HfSiON layer, a ZrSiO layer, a ZrHfO layer, a LaCoO layer, and a TiSiN layer. 20

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FIG. 1 (PRIOR ART)

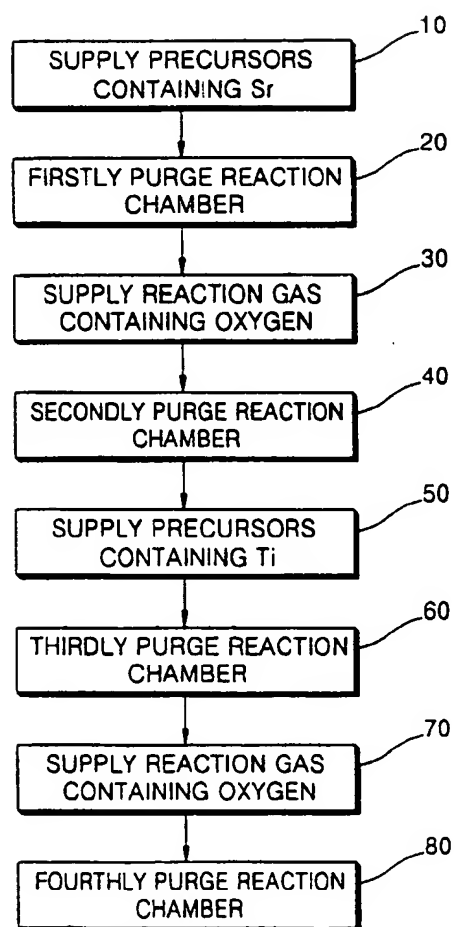


FIG. 2 (PRIOR ART)

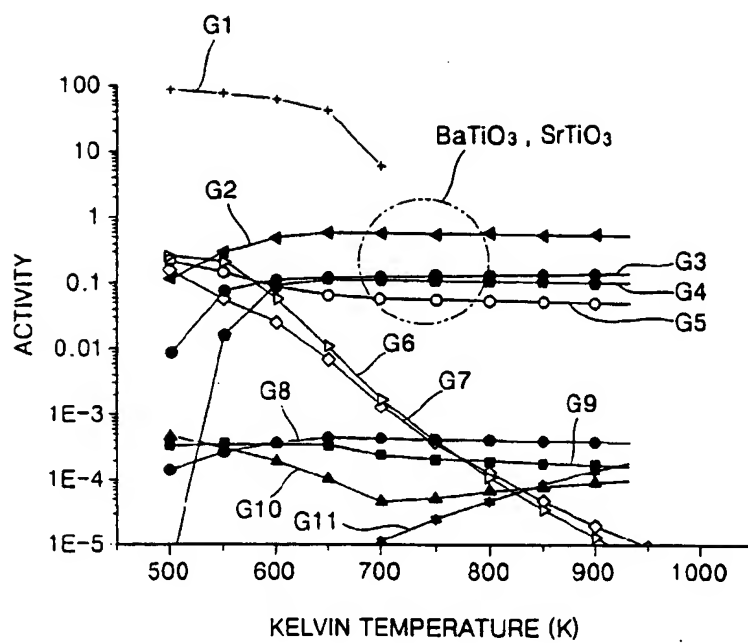


FIG. 3

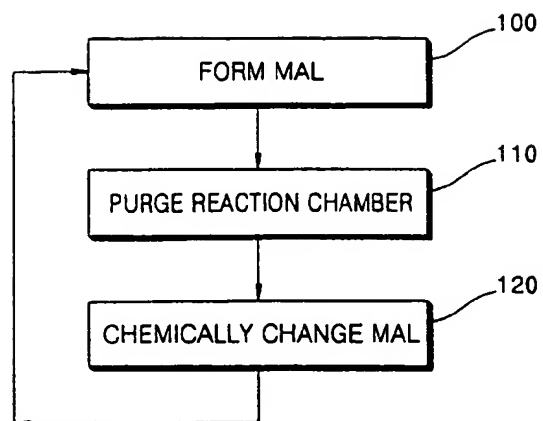


FIG. 4A

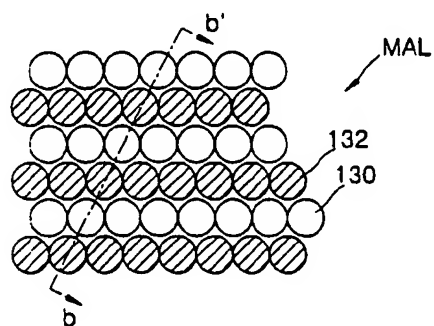


FIG. 4B

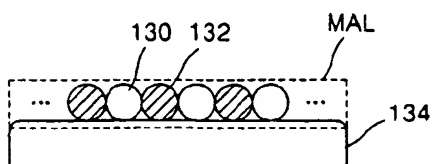




FIG. 5

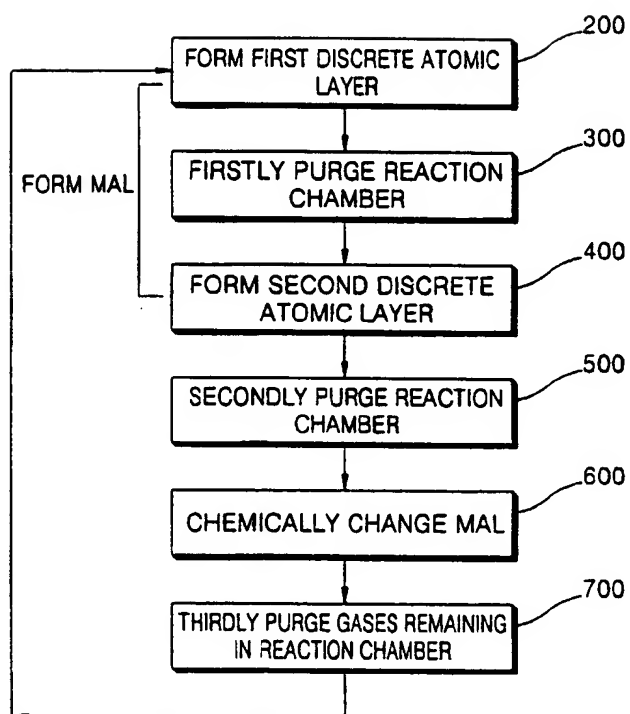


FIG. 6A

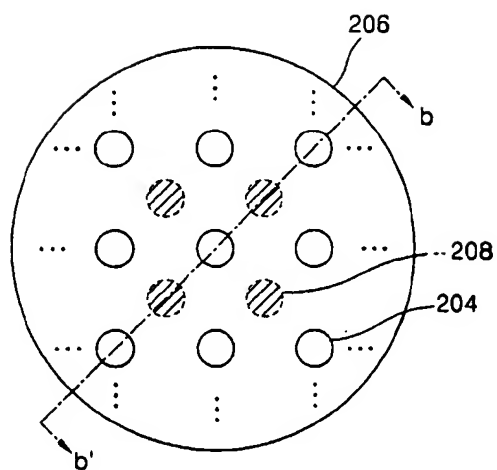


FIG. 6B

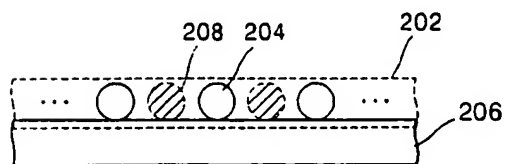


FIG. 7

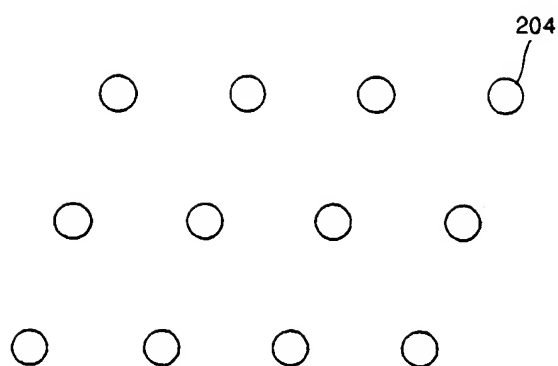


FIG. 8

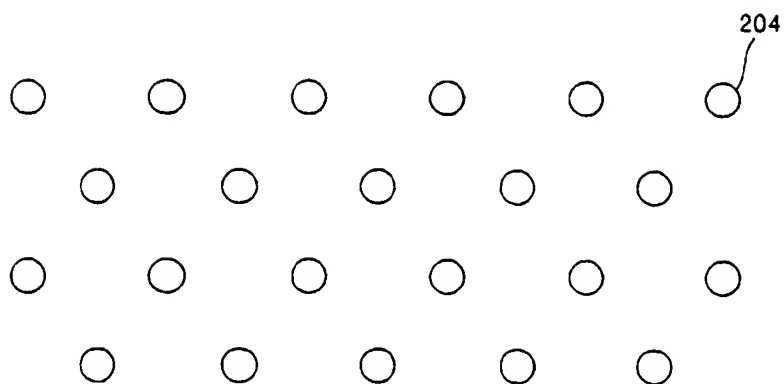


FIG. 9A

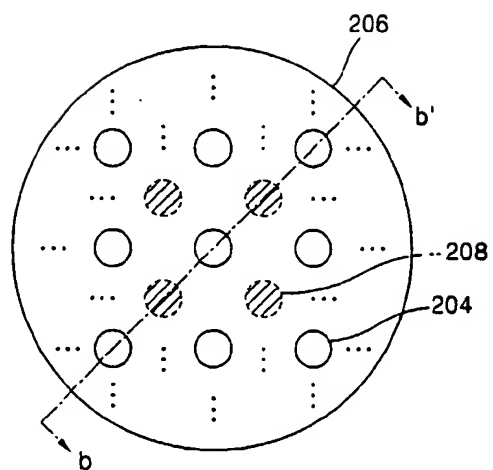


FIG. 9B

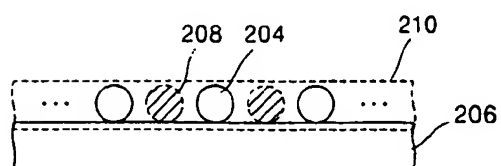


FIG. 10A

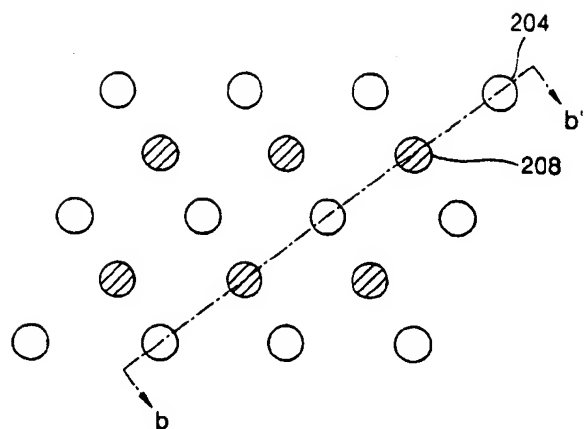


FIG. 10B

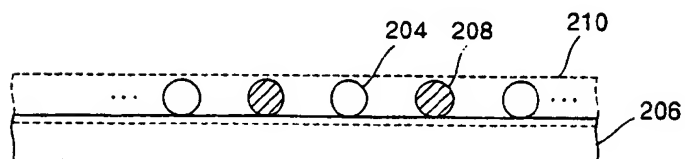


FIG. 11A

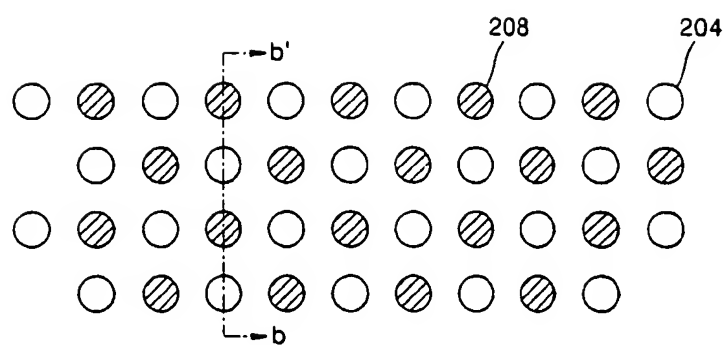


FIG. 11B

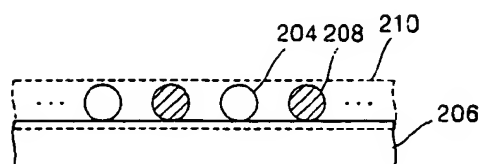


FIG. 12

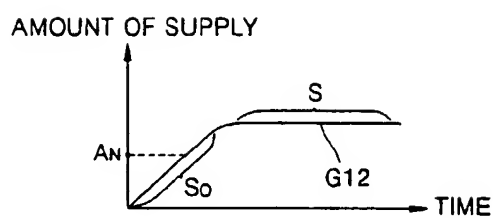


FIG. 13

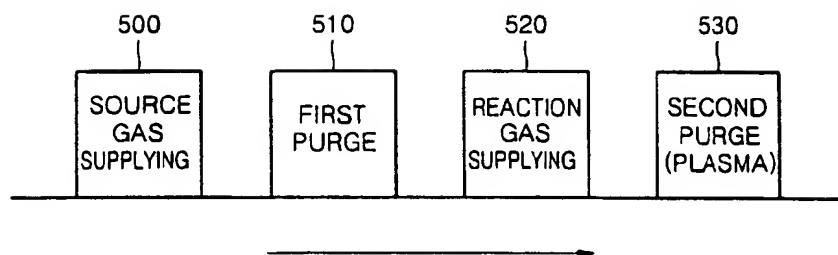




FIG. 14

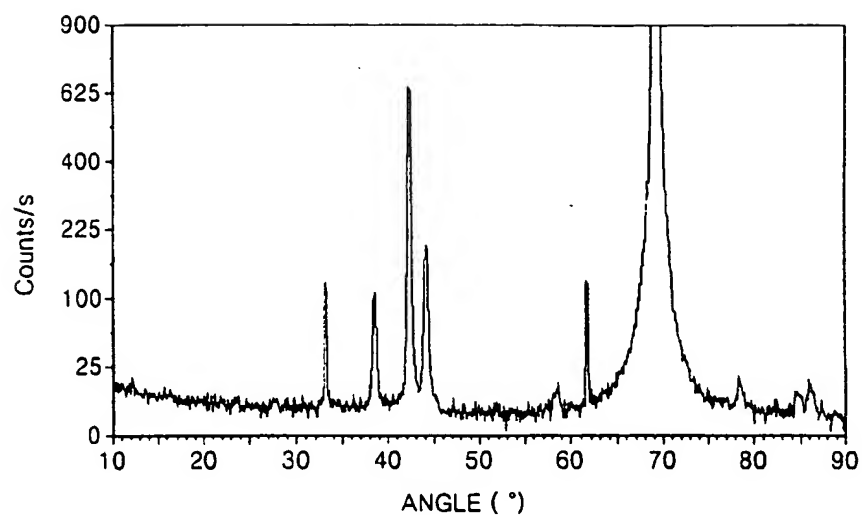


FIG. 15

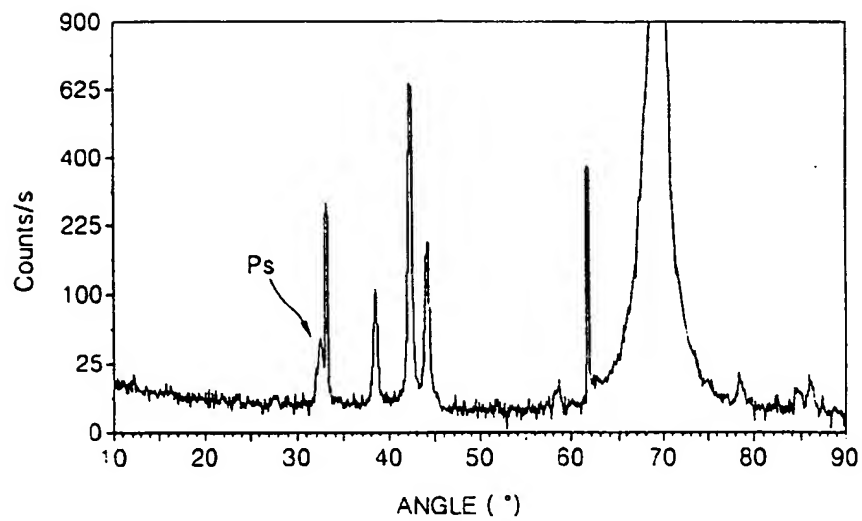


FIG. 16

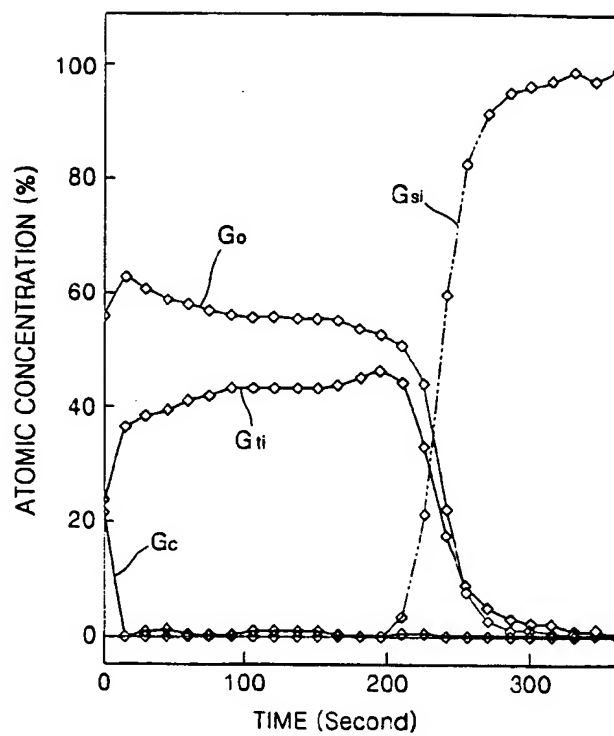


FIG. 17

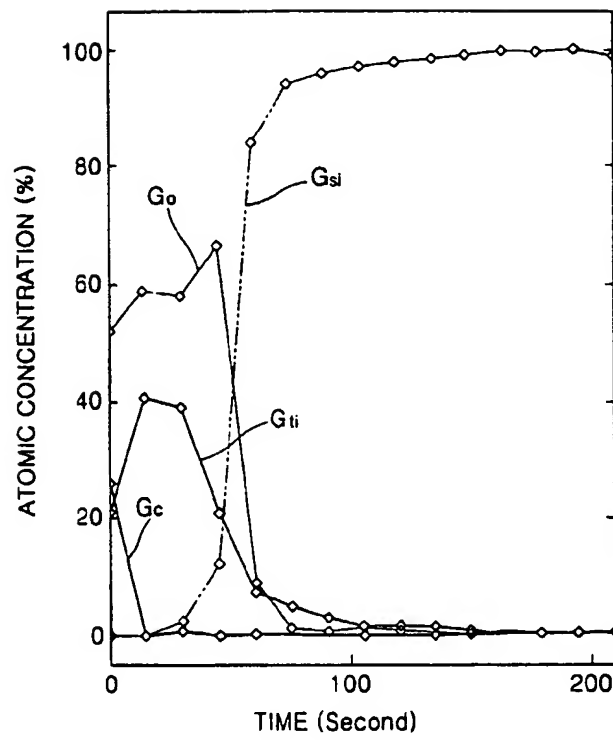


FIG. 18

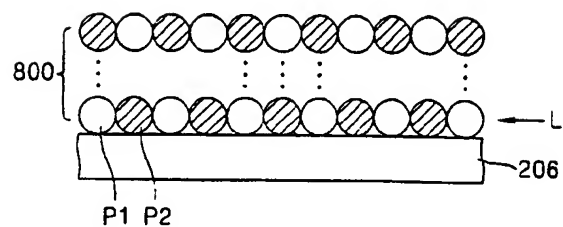


FIG. 19

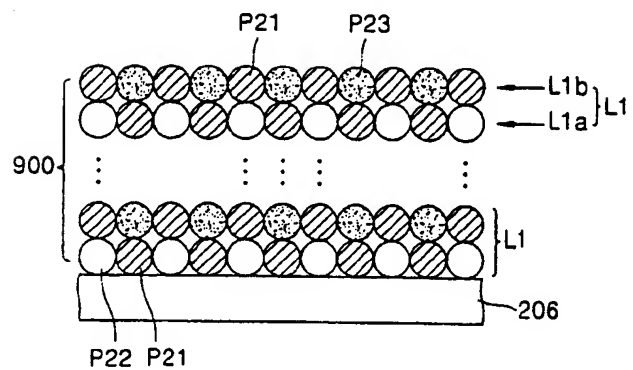
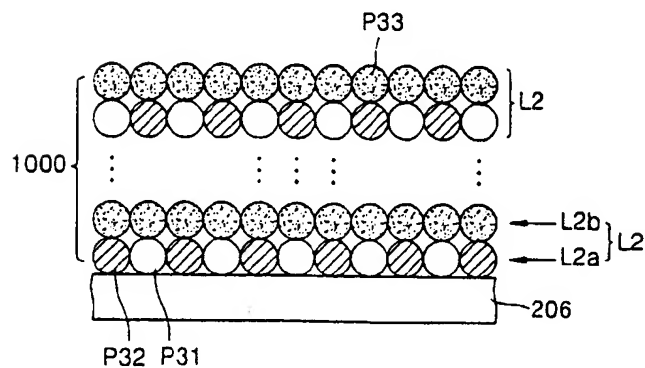
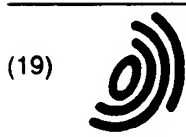


FIG. 20





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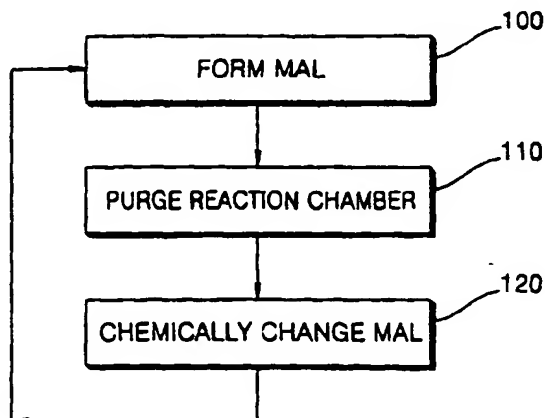
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(54) **Thin film including multi components and method of forming the same**

(57) A thin film including multi components and a method of forming the thin film are provided. A substrate is loaded into a reaction chamber. A unit material layer is formed on the substrate. The unit material layer is a

mosaic atomic layer composed of two kinds of precursors containing components constituting the thin film. The inside of the reaction chamber is purged. The MAL is chemically changed.

**FIG. 3**





European Patent  
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# EUROPEAN SEARCH REPORT

Application Number  
EP 02 25 3123

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Place of search THE HAGUE		Date of completion of the search 11 March 2004	Examiner Castagné, C
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document</p> <p>T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons &amp;: member of the same patent family, corresponding document</p>			

**ANNEX TO THE EUROPEAN SEARCH REPORT  
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